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The Determination of Carbon
In Iron and Steel

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THE DETERMINATION OF CARBON
IN IRON AND STEEL

BY

GERTRUDE NIEDERMAN

THESIS

For the Degree of Bachelor of Science

in Chemistry

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

GERTRUDE NIEDERMAN

ENTITLED THE DETERMINATION OF CARBON IN STEEL

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

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THE DETERMINATION OF CARBON IN IRON AND STEEL.

Carbon exists in steel in different chemical forms, according as the latter is hardened or not. This is seen from the different action that dilute acids have upon steel under these two different conditions. When hardened steel is treated with sulphuric acid (one part of sulphuric acid in ten parts of water) a part of the carbon is evolved as hydrocarbons, the rest remains as a residue.(1) The carbon that is transformed into hydrocarbons is called "hardening" carbon. The residue is called carbide carbon. Besides these two forms, there are many compounds of carbon found in steel, (2) all of which have some effect on the steel not only in its physical properties, but also on the procedure in its analysis. The chemist, therefore, who undertakes the problem of steel analysis is confronted with many obstacles because he does not work with definite compounds. Very much of his work is done in darkness because very little is as yet known about the different compounds in which carbon exists in steel. This problem becomes more serious when we stop to think of how much depends on the accurate analysis of carbon in steel, that a difference of 0.1 per cent of carbon makes a difference of several thousand pounds in the strength of the steel (2).

Professor Ackerman (3) states that carbon exists in three forms and not in two as has been previously thought; and that it is to the third intermediate condition of carbon that the phenomenon of hardening and tempering of steel is due; that when steel is gradually cooled, this intermediate carbon travelled toward the graphitic carbon; and that this explains the striking changes that take place when an ingot of steel is hardened and then

subjected to the process of hammering and rolling. These relations between the physical and chemical properties of steel have been worked out to a great extent by Baron von Jüptner.(4) The effect of carbon is most marked. As the percent of carbon is increased up to 4.3%, the melting point of the steel diminishes. Beyond this point of carbon content, the melting point again rises. The specific heat increases with the percentage of carbon; while the tensile strength increases with an increase in carbon up to a certain limit when it begins rapidly to diminish; the maximum strength seems to be attained with a carbon content of .9%. The malleability and weldability diminish with increase of carbon. The hardening capacity increases with increase of carbon reaching a maximum when the steel contains 2% of carbon.

Moreover the properties of the steel depend on the form of the carbon. Graphite, diamond and temper carbon affect the mechanical properties of iron only in so far as the mass of the metal in a given cross section is diminished. Graphite increases the quantity ^{of heat} necessary for its fusion. Hardening carbon increases the tensile strength, limit of elasticity and hardness. Carbide carbon acts just opposite to hardening carbon.

To show the difficulties met with in the analysis of steel, it may not be out of place at this point to mention the other constituents of steel. Phosphorus occurs as Fe_3P and as Mn_3P_2 . This is known as indifferent or phosphide phosphorus; both are insoluble in acids. The other known as "dangerous" or "hardening" phosphorus, is disseminated through the mass of the metal and escapes as PH_3 when treated with dilute acids. The other impurities also exist in at least two forms, and consequently exert different influences according to which form is present.

Chromium occurs in two different forms - (1) dissolved throughout the mass of the iron and, therefore, soluble with it in acids; (2) separated in the form of acicular crystals which are attacked only with difficulty by acids. These acicular crystals are chromium iron carbides, the composition of which varies with the per cent of chromium present. Up to now the compounds Cr_3FeC_3 , and $\text{Cr}_2\text{Fe}_7\text{C}_3$ have been determined. (4). Tungsten and molybdenum occur as Fe_2W or Fe_3W and as Fe_3Mo_2 respectively. Sulphur (4) is present in several forms, (1) as a compound which yields hydrogen sulphide on treatment with dilute acids; (2) as a compound which yields the volatile $\text{S}(\text{CH}_3)_2$ with dilute acids; and (3) in a form which remains behind as an insoluble, organic residue. The last two may, however, represent decomposition products of one and the same compound. Manganese, nickel, copper and titanium seem to occur in the dissolved form, but a part of the manganese may occur as a silicide or sulphide (4).

There are many methods for the analysis of carbon in steel, but two are used most at the present time. The wet combustion method (4) had been used much before the direct combustion was worked out. The former consisted in treating the steel with sulphuric acid in a closed flask, thus liberating the hydrocarbons, which are then burned to carbon dioxide and measured volumetrically. This method has been improved upon by adding chromic acid along with the sulphuric acid, thus preventing the formation of liquid hydrocarbons and a carbonaceous residue. The gases in this method may be directly passed into the absorbing apparatus. As the formation of hydrocarbons occurs at the beginning of the operation, this may be prevented by mixing the

steel with metallic mercury or phosphoric acid. This protects the steel until a high temperature is reached. This method is very practicable when a great many samples have to be analysed, in a day. But where great accuracy is required, this process can not be used; for in spite of the great precautions taken, there is still a loss from the formation of liquid hydrocarbons.

Anchy (5) says that in wet combustion there is no method in use, in which all the moisture is absorbed before reaching the carbon dioxide absorber; this is due to the brisk and continuous passage of the gas evolved from the carbon in this method. Moreover, this method is known to be unsuited for graphite determinations, because some of the graphite is oxidized to merely carbon monoxide.

Another method used sometimes is the Eggerts color process. This is accurate enough for ordinary steel works and is used where many samples have to be determined in a short time. But unless conditions are carefully observed, the method is very inaccurate.

Some of these conditions are:-

1. Rate of solution.
2. Color is bleached by daylight.
3. In hardened steel there exists a form of carbon which is not affected by the color of nitric acid.
4. The color is destroyed by continued heating, and consequent evolution of carbon dioxide.
5. The color is influenced by the amount of Si, P, and Cr. present.

The most accurate methods for carbon analysis are those methods in which the carbon is liberated and then burned to carbon dioxide; and the direct combustion method.

There are many ways of liberating the carbon. Binks and Weyl (7) liberate the carbon by making a rod of steel the anode in a sulphuric acid solution, thus dissolving the iron and leaving the carbon behind. This method is inconvenient, and takes a long time. Another method is liberating the carbon by volatilizing the iron in a stream of chlorine. (7). The chlorine must be dry and free from oxygen, and is, therefore, passed over heated charcoal before reaching the steel. The most extensively used and most accurate method is that of dissolving out the carbon by means of solutions of reducible metallic salts. At first copper sulphate was used for this purpose, but it took too long to redissolve the insoluble cuprous salts formed in this way; so that a double salt of the chlorides of copper and of sodium, potassium, or ammonium was substituted. Ammonium chloride, however, can not be obtained free from pyridine, so that the double salt of potassium chloride and copper chloride is now used exclusively. (7) This solution made slightly acid, is found to give higher results than the neutral solution; this may be due to the fact that neutral solutions may dissolve some of the carbonaceous residue. (8) But a great excess of acid should be avoided as it would also result in the evolution of hydrocarbons¹. Some of the disadvantages of this method, are that some of the carbide carbon in this method is lost by contact with dilute acids and by contact with the moist oxygen in the water and the air. There may also be some error due to drying the carbon; for when carbon containing moist oxygen, is dried at 100° it gives carbon dioxide. Heating the solution above 100° C. should be avoided since hydrocarbons are evolved above that temperature.

The separated carbon has been, at times determined by

oxidizing it by means of H_2SO_4 and chromic acid. But it has been shown by the researches of C.F. Cross and J. Widmer (10), and by J. Kjeldahl (11) that not all the carbon is oxidized by this method to carbon dioxide.

Sargent (12) uses the solution method, and then burns the liberated carbon in a stream of oxygen, using an ordinary three burner combustion furnace.

Another method of burning the carbon residue is that of burning it in the Shiner crucible (13). This consists of a platinum crucible having a platinum cooling chamber; the latter closes the crucible tightly by means of a rubber band

The simplest method of determining carbon in iron and steel is by direct combustion. This method seems to have been originated by Berzelius and Mulder (14). Combustion by this method, however, takes place only at a very high heat, and in a finely divided state of the metal. To obviate these two difficulties, many of the investigators mixed the metal with some oxidizing agents, which would aid the complete combustion of carbon. Richard Lorenz (14) covered the steel with lead chromate and heated it in a porcelain tube. This method is very inconvenient, because the porcelain tube cannot stand the high heat necessary, and is, moreover, attacked by the oxidizing agents. Dr. Mulder (15) shows that lead chromate can not affect the complete combustion of carbon, especially in the graphitic state. He also shows that M. Kndernatch's method of effecting combustion with oxide of copper without a current of oxygen is incomplete. Otto Petterson and August Smith (16) fuse steel in a bent hard glass tube with potassium pyrosulphate. The sulphur dioxide formed passes over crystals of chromic acid, and then over copper oxide which is moderately heated, and which completely absorbs the sulphur dioxide. The carbon dioxide is collected in pure, clear, baryta water. The barium carbonate is then decomposed and the carbon dioxide determined volumetrically. A.A. Blair (17) adds pure potassium acid sulphate to the sample in a platinum boat which is placed in a larger boat. A cover is placed over the larger so that any of the fused mass spiring up, does not get into the combustion tube. He uses plugs made of pumice, and wrapped with platinum foil. These are pushed in after the boat. The combustion is made in a slow current of oxygen. The sulphuric acid fumes condense in a tube containing beads; the gases are then passed into

flasks kept hot and containing a solution of chromic acid in sulphuric acid to retain any sulphur dioxide fumes. The carbon dioxide after passing over pumice stone saturated with chromic acid, and over calcium chloride, is absorbed and weighed.

But the simplest, method of determining carbon is burning the steel direct in a stream of oxygen (18). Rosyetti (19) states that carbon can be determined that way in less than an hour. He mixes the metal with alumina in a porcelain boat. A porcelain combustion tube is used. This is connected on one side with a glass tube containing copper oxide, which is previously heated, and with absorption apparatus. B. Blount (20) used a porcelain tube. He heated the metal to 700-800° C. in a stream of oxygen. He found that the carbon dioxide is formed at first very rapidly, but that a layer of oxide soon forms over the molten metal, which prevents further oxidation. He then used a litharge flux to prevent the formation of an oxide film, but no tube used could resist the action of the litharge. But he found that if he raised the temperature to 1100°- 1200° C., three to five grams of the filings are completely burned within an hour. The porcelain tube, however, cannot stand the high temperature for long, and often fractures during the experiment. Jabonlay (18) heats the steel in an electric furnace, and in case of more refractory metals, as ferro-chrome iron, he mixes the material with bismuth oxide. Dr. E. Mulder (15) fills two thirds of the combustion tube with sand which has been heated to redness in a stream of oxygen; he next introduces a plug of asbestos and the cast iron mixed with pumice stone; then another plug of asbestos; a layer of copper oxide; and then closes it with another plug of asbestos. He heats this with oak charcoal.

The Solution Method.

In the work in this laboratory the method of dissolving the steel in a slightly acid solution of the double chloride of potassium and copper, and burning the released carbon in an ordinary combustion furnace was compared with the method of burning the metal direct in a stream of oxygen. Before beginning the work on carbon, however, a sample of steel was analyzed as to its principal constituents.— Silicon, phosphorus, manganese and sulphur. Besides this preliminary work, a sample of urea was analyzed as to its carbon and hydrogen content, so as to have some check on the work on carbon in steel.

Silica was determined by double evaporation and filtration after dissolving the sample in nitric acid. Phosphorus was determined in the same sample with silica after the latter was removed. The method used was the precipitation of the phosphorus with ammonium molybdate as ammonium phospho-molybdate. This precipitate was dissolved in strong ammonium hydroxide and the phosphorus was reprecipitated with magnesia mixture as magnesium ammonium phosphate. This precipitate was ignited and weighed as magnesium pyrophosphate. The solutions of ammonium molybdate and magnesia mixture were prepared according to Blair's "Iron and Steel Analysis".

Manganese was determined by Noyes' method. The manganese by this method is precipitated as the dioxide by oxidizing the manganese in a sodium acetate solution with bromine water. The manganese dioxide is then dissolved by a standard solution of ferrous ammonium sulphate. The excess of ferrous ammonium sulphate is then titrated against a standard permanganate solution.

The steel for this determination is dissolved in nitric acid and the iron is precipitated with a sodium carbonate solution and zinc oxide emulsion. The potassium permanganate used was standardized by crystallized oxalic acid, sodium oxalate, and Kahlbaum C.P. ferrous ammonium sulphate, the last two giving excellent results. The ferrous ammonium sulphate was standardized by means of the above potassium permanganate.

Sulphur was determined by the evolution and by the gravimetric method. In the evolution method, the steel is treated with a mixture 1 part of strong HCl and one part of water. The evolved H_2S is absorbed in a KOH solution. The hydrogen sulphide after acidifying is then oxidized with an excess of iodine solution. The excess of the iodine solution is determined by titrating against a standard sodium thiosulphate solution.

In the gravimetric method, the steel was dissolved in nitric acid; the silica was precipitated as $BaSO_4$ and weighed in that form.

The results of the analyses is given below:-

Mn.	P.	Si.	S. (gravimetric)	S. (evolution)
.94%	.107%	.081	.0772%	.0756%
.95%	.110%	.084	—	.0709%
.96%				.0748% .0751% .0765% .0753%

The carbon and hydrogen in urea were determined in an ordinary combustion furnace, using a hard glass tube (Jena glass) and a porcelain boat. The purifying chain consisted of soda lime towers followed by calcium chloride towers. The preheater was found to be unnecessary. The absorption chain consisted of a soda lime tube, another tube one arm of which is filled with soda lime (the arm connected with the soda lime tube) and the

other arm with calcium chloride; this is followed by a calcium chloride tube, and finally by a safety tube. The results obtained are as follows:-

<u>Found.</u>	<u>Theoretical.</u>		
C.	H_2	C.	H_2
20.5%	6.22%	19.97%	6.65%
20.17%	6.62%		
20.04%	6.50%		
20.01%	6.50%		

The solution of the double chloride of copper and potassium was prepared according to the directions given in Blair's "Chemical Analysis of Iron and Steel". In each case a sample of 2-3 grams was dissolved in 300 cc. of the solution, to which 10 cc. strong HCl had been added. The stirring was done by a motor. The filtration was done by the apparatus shown in Fig. 1.

"A" is a 500 cc. flask the bottom of which is cut off. "d" is a perforated porcelain disk, through the holes of which passes a platinum wire. The wire is fused to the glass rod "c" which is long enough to reach the bottom of the filter flask, supporting the disk. The porcelain disk is covered with a layer of asbestos. Above this is placed another disk and again some asbestos. The residue is washed with dilute HCl and then with pure water. It is then dried in an oven at 100° C. and burned in the same manner as the urea was burned above. The purifying and the absorption apparatus is also essentially the same, except that in this case a solution of chromic acid, a tube containing anhydrous copper sulphate and another tube containing calcium chloride precede the

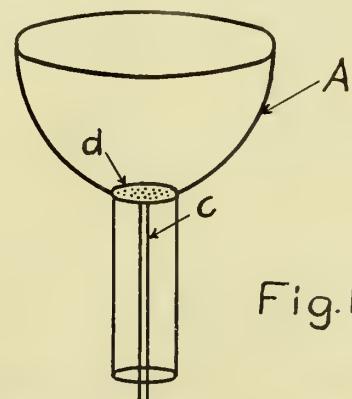


Fig. 1.

soda lime tubes. The first two serve to absorb all sulphur dioxide and chlorine, the last to absorb all the moisture that may not have been absorbed by the copper sulphate. A preheater is also used. This consists of a glass tube containing platinized asbestos, and ^{is} heated slightly.

The use of the soda lime U tubes is found to be much more desirable than that of the Geissler potash bulb, because on the comparatively small surface of the former, a constant weight can be obtained with much less difficulty, and because the U tube is more convenient to handle than the potash bulb; moreover, it is not difficult to tell when the tubes become inefficient because the soda lime turns white on absorption of carbon dioxide. The soda lime was prepared according to the directions given in Benedict's "Elementary Organic Analysis". The tubes are rubbed clean with a linen cloth and allowed to stand in the balance room 20 - 30 min. before each weighing.

The sample used was a Bessemer steel. The results obtained were as follows:-

0.447%	0.446%	0.448%
0.442%	0.444%	0.445%

The last two samples were allowed to stand for three days before filtering.

Direct Combustion.

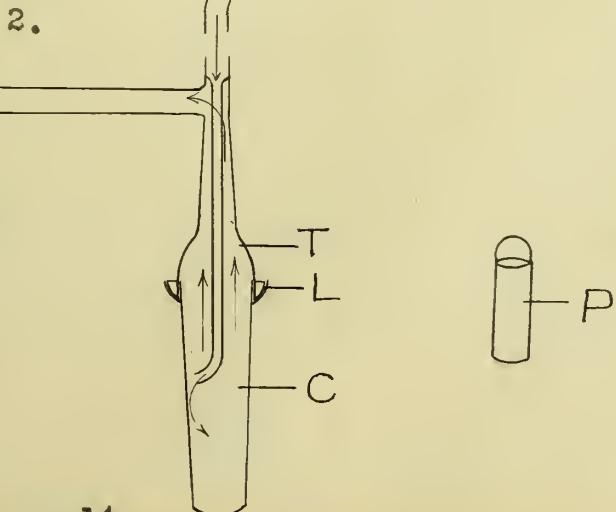
The direct combustions were at first carried on in a platinum tube about one foot in length, and an inch in diameter. Lead coils through which circulated cold water, surrounded the ends of the tube. About one inch from each end within the tube was placed a porcelain disk, which rested upright on a bent platinum wire. These disks checked somewhat the radiation of the heat, i.e. they reflected the heat and thus kept it from reaching the rubber corks

used at each end of the tube. The purifying and absorption apparatus is the same as that used in the solution method above except that the gases passed through slightly heated platinized asbestos before passing through the absorption tubes. The chromic acid in this case was saved and analyzed for sulphur. The results obtained by this method are as follows:-

Carbon in Original Sample.	Carbon in Residue.
.394	.460
.421	.406

The residues of the burned steel were then pounded in a steel mortar, thus pulverizing the burned steel and leaving the unburned behind; the latter was separated from the pulverized Fe_3O_4 by means of a sixty mesh sieve; the carbon in it was then determined by the solution method. The result is given in column As is seen from the above figures, the technique in this process is not good. It is impossible to keep the corks from becoming hot, even by the use of the disks and by wrapping the ends of the tube with asbestos. Furthermore it is impossible to concentrate all the heat on the steel.

The platinum Gooch, (figure 2) crucible which is used for water determination, was then tried.



This consists of the crucible proper "C" which ends in the flanged lip L. "T" is the cap which fits tightly on the crucible. "P" is a platinum pail which carries the steel.

Manipulation:- The pail "P" is filled with finely powdered alumina, free from sulphur and all organic matter. A hole is then bored in the alumina by means of a glass rod. Into this hole is placed the sample of steel. Care should be taken not to make this hole too large and not to take too large a sample as it is hard to get the burned steel out. The bottom of the crucible "C" is also covered with alumina before the pail is placed into it, so that the latter does not fuse to the former. The purpose of the alumina is to keep the steel from touching the platinum pail. In the lip "L" is placed pure powdered, sodium tungstate. When the pail with the sample has been placed into the crucible, the cap is fitted on and the sodium tungstate is heated till it melts; a slight pressure is then applied to the top and bottom of the crucible. The sodium tungstate is allowed to solidify, and the crucible is sealed. "A" and "B" are glass tubes fused to the platinum tubes n₁ n₂. A is connected with the purifying chain "B" with the absorption chain. The full heat of the blast is then applied to the crucible where the pail is situated. The combustion is complete in 15 minutes. Oxygen is passed throughout the combustion, and is displaced at the end by passing air through the tubes for 10 - 15 minutes. The purifying and absorbing chain is the same as described above in connection with the platinum tube, but instead of using chromic acid for absorbing the sulphur, barium chromate was used. The results obtained by this method are as follows:-

.443%	.449%
.445%	.454%
.444%	.447%

This method is very simple and is accurate for all common purposes. It gives as high and a little higher results than the solution method gives. The advantages and disadvantages of this method have been given above.

As was mentioned above, the purpose in this work was to analyze sulphur at the same time, by collecting the SO₃ formed in BaCrO₄, but the results obtained were very low. We concluded that the alumina absorbed some of the SO₃; we therefore attempted to substitute silica for alumina; but the silica did not allow of too high heating, the results were, therefore, all too low.

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